Monoclinic EuSn$_2$As$_2$: A Novel High-Pressure Network Structure

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The layered crystal of EuSn$_2$As$_2$ has a Bi$_2$Te$_3$-type structure in rhombohedral ($R$$\bar{3}$m) symmetry and has been confirmed to be an intrinsic magnetic topological insulator at ambient conditions. Combining ab initio calculations and in situ x-ray diffraction measurements, we identify a new monoclinic EuSn$_2$As$_2$ structure in C$2$/m symmetry above $\sim$14 GPa. It has a three-dimensional network made up of honeycomblike Sn sheets and zigzag As chains, transformed from the layered EuSn$_2$As$_2$ via a two-stage reconstruction mechanism with the connecting of Sn-Sn and As-As atoms successively between the buckled SnAs layers. Its dynamic structural stability has been verified by phonon mode analysis. Electrical resistance measurements reveal an insulator-metal-superconductor transition at low temperature around 5 and 15 GPa, respectively, according to the structural conversion, and the superconductivity with a $T_c$ value of $\sim$4 K is observed up to 30.8 GPa. These results establish a high-pressure EuSn$_2$As$_2$ phase with intriguing structural and electronic properties and expand our understandings about the layered magnetic topological insulators.

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Topological insulators have attracted much research interest due to their novel band structure and quantum phenomenon [1–7]. In the past few years, a good deal of attention has been focused on the intrinsic magnetic topological insulators because the interaction between magnetism and topological surface states can produce many exotic topological quantum effects, such as the quantum anomalous Hall effect, Majorana bound states and axion insulator states [8–21]. Recently, EuSn$_2$As$_2$ has been confirmed to be an intrinsic magnetic topological insulator by combining first-principles calculation and angle resolved photoemission spectroscopy measurements [14]. EuSn$_2$As$_2$ crystallizes in a Bi$_2$Te$_3$-type structure in rhombohedral ($R$$\bar{3}$m) symmetry and consists of SnAs bilayers sandwiched by six coordinated Eu cations via van der Waals bonding. The weak van der Waals force between the bilayers allows EuSn$_2$As$_2$ to be readily exfoliated into few layer sheets [22]. Meanwhile, magnetic susceptibility measurements suggested that EuSn$_2$As$_2$ undergoes an antiferromagnetic (AFM) transition with Neel temperature $T_N \sim 24$ K, where the Eu$^{2+}$ ions are coupled ferromagnetically within each layer and antiferromagnetically across the adjacent SnAs bilayers, forming an A-type AFM order [14,22].

Pressure, as a basic thermodynamic parameter, plays an important role in the research of topological materials, and can effectively tune the crystal and electronic structure of material to form a new state of matter. The pressure-induced superconductivity has been successfully observed in the typical topological insulators Bi$_2$Se$_3$ [23,24], Bi$_2$Te$_3$ [25–28], and Sb$_2$Te$_3$ [29], which crystallize in a rhombohedral structure at ambient pressure and undergo structural phase transitions toward a monoclinic phase under high pressure [30]. The structural transitions mostly correspond to the appearance of different superconducting phases or $T_c$ mutations, illustrating the inevitable correlation between structure and superconductivity [24,25,31–36]. Meanwhile, EuSn$_2$As$_2$ has a similar Bi$_2$Te$_3$-type layered structure in rhombohedral symmetry under ambient pressure, however, a systematic high-pressure study on EuSn$_2$As$_2$ is still lacking.
In this Letter, we present a comprehensive study on the structural phase transition and electrical transport property of EuSn$_2$As$_2$ under a wide pressure range of 0–30 GPa. Combining ab initio calculations and in situ x-ray diffraction measurements, we identify a monoclinic EuSn$_2$As$_2$ phase in C2/m symmetry above ~14 GPa. This new-type monoclinic phase has a network structure comprising honeycomb-like Sn layers and zigzag As chains and can be transformed from the layered rhombohedral structure via a two-stage reconstruction mechanism with the connecting of Sn-Sn and As-As atoms successively between the buckled SnAs layers. Its dynamic structural stability has been verified by phonon mode analysis. Detailed electrical resistance measurements reveal an insulator-metal-superconductor transition at low temperature around 5 and 15 GPa, respectively, correspond to the structural conversion process. These results show a strong correlation between the structure and electrical transport property under pressure.

Our density functional theory (DFT) calculations are performed using the Vienna ab initio simulation package [37] with the projector augmented wave method [38]. The Perdew-Burke-Ernzerhof revised for solids [39] exchange-correlation functional is adopted for the evaluation of structural and magnetic stability of EuSn$_2$As$_2$ under pressure. The valence states 5s$^2$6s$^2$5p$^4$4f$^7$ for Eu, 5s$^2$5p$^2$ for Sn, and 4s$^2$4p$^3$ for As are used for the plane wave basis set. To match the energy position of Eu 4f bands in the experiments [14], the Hubbard U = 5 eV is used to treat the localized 4f electrons of Eu in the DFT + U scheme [40]. Phonon calculations are performed using the PHONOPY package [41]. Meanwhile, our in situ high-pressure experiments are performed in a diamond anvil cell with cuvet size of 300 μm in diameter. The synchrotron x-ray diffraction (XRD) patterns are collected with wavelength of 0.6199 Å and integrated using FIT2D software [42]. The electrical resistance measurements are established by the standard four-probe methods at the

![Image](108x153 to 393x271)

**FIG. 1.** (a) α-EuSn$_2$As$_2$ in rhombohedral $R\bar{3}m$ (No. 166) symmetry at 0 GPa with four buckled As-Sn layers and two Eu layers. (b) α-EuSn$_2$As$_2$ in rhombohedral $R\bar{3}m$ symmetry at 10 GPa with the connecting of Sn-Sn atoms between the nearest neighbor SnAs layers. (c) β-EuSn$_2$As$_2$ in monoclinic $C2/m$ (No. 12) symmetry at 20 GPa with the connecting of As-As atoms between the SnAs layers across the Eu layers. It has a network structure comprising honeycomblike Sn sheets and zigzag As chains. The magnetic unit cell in $P2/m$ (No. 10) symmetry is marked with dashed lines. (d) Top view of the honeycomblike Sn sheet in (c). (e) Relative enthalpy between the α- and β-EuSn$_2$As$_2$ phases as a function of pressure.
the Eu atoms. The calculated magnetic moments on Eu sites are 6.92–6.98 $\mu_B$ due to the 4 $f$ electrons. The lattice parameters at 20 GPa in $P2_1/m$ symmetry are estimated to be $a = 7.659$, $b = 3.596$, $c = 6.958$ Å, and $\beta = 87.33^\circ$, occupying 1 $a$ (0.0, 0.0, 0.0)-Eu1, 1 $h$ (0.50, 0.50, 0.50)-Eu2, 2 $m$ (0.3882, 0.0, 0.1704)-Sn1, 2 $n$ (0.8882, 0.5, 0.6704)-Sn2, 2 $m$ (0.7860, 0.0, 0.3730)-As1, and 2 $n$ (0.2860, 0.5, 0.8730)-As2 Wyckoff positions. In order to confirm the dynamical stability, we have calculated the phonon band structures and partial density of states (PDOS) in $P2_1/m$ symmetry at 20 GPa. As shown in Fig. 2, the high frequency modes around 200 and 140 cm$^{-1}$ are mainly contributed by As atoms, while the low frequency modes around 55 cm$^{-1}$ are mainly contributed by Sn atoms. Throughout the entire Brillouin zone, no imaginary frequencies are observed, confirming the dynamic stability of this new $\beta$-EuSn$_2$As$_2$ phase.

Figure 3(a) shows the experimental XRD patterns of EuSn$_2$As$_2$ up to 30.7 GPa at room temperature. In the low-pressure range below 11 GPa, no obvious structure changes are observed in the XRD patterns, indicating that the rhombohedral $\alpha$ phase persists up to 11 GPa. With increasing pressure to 12.6 GPa, two new notable diffraction peaks at 14–15$^\circ$ appear and gradually higher with further compression, manifesting the occurrence of a structural phase transition. Meanwhile, the main peaks of $\alpha$ phase around 12$^\circ$ and 17$^\circ$ gradually weakened and almost disappeared at 23.4 GPa, indicating the phase transition almost completely achieves around 23.4 GPa. In order to get the best understanding of the experimental data, we have refined the powder XRD pattern by Rietveld method [46] through the FullProf software [47]. At 0.16 GPa [see Fig. 3(b)], almost all of the diffraction peaks can be well indexed to the rhombohedral $\alpha$ phase with space group $R\bar{3}m$, except for tiny diffraction peaks which are attributable to the residual Sn flux with a small weight fraction of $\sim$0.59% (see Fig. S1 in Supplemental Material [44]). Based on our proposed monoclinic $\beta$-EuSn$_2$As$_2$ structure and the simulated XRD patterns [see Fig. 3(e)] at 20 GPa and

![FIG. 2. Phonon band structures and PDOS for $\beta$-EuSn$_2$As$_2$ at 20 GPa in a monoclinic ($P2_1/m$) magnetic primitive cell.](image-url)

![FIG. 3. (a) The in situ XRD patterns of EuSn$_2$As$_2$ under 0.16–30.7 GPa. The synchrotron x-ray wavelength $\lambda = 0.6199$ Å. (b)–(d) The refined XRD patterns at 0.16, 15.6, and 27.8 GPa. The blue, green, and pink vertical tick markers are corresponding to the Bragg reflections of $\alpha$ phase, $\beta$ phase, and Sn, respectively. (e) Simulated XRD patterns of the $\beta$ phase at 20 GPa. The two main peaks correspond to the new diffraction peaks in (a) above 12.6 GPa.](image-url)

![TABLE I. Calculated lattice parameters at 0, 10, and 20 GPa for $\alpha$-EuSn$_2$As$_2$ in rhombohedral ($R\bar{3}m$) and $\beta$-EuSn$_2$As$_2$ in monoclinic ($C2/m$) symmetry, compared to our and the reported experimental data [22] at 0.16, 11, and 18.8 GPa.](table-url)
positions are given in Table S1 in Supplemental Material [44]), compared to available experimental data [22].

We next discuss the electronic properties at low and high temperature range. Figures 4(a)–4(c) plot the resistance (R) of EuSn₂As₂ single crystal as a function of temperature under various pressures up to 30.8 GPa. For 0.77 ≤ P ≤ 3.08 GPa, at low temperature below Tₐ [see Fig. 4(a)], the resistance increases with the decrease of temperature, exhibiting an insulating behavior. For 4.93 ≤ P ≤ 7.77, resistance increases first around Tₐ, reaches a maximum then followed by a slight drop upon further cooling, exhibiting a metal-like behavior. With increasing pressure above 9 GPa [see Fig. 4(b)], the resistance decreases distinctly with decreasing temperature, exhibiting a typical metallic behavior below Tₐ. More interestingly, a superconducting transition with onset temperature Tₐ ∼ 4 K is observed at 15.2 GPa [see Fig. 4(c)]. The superconductivity persists up to 30.8 GPa with Tₐ maintaining a constant value ∼4 K. To corroborate the superconductivity, we have also measured the temperature dependent resistance with various external magnetic fields (see Fig. S3 in Supplemental Material [44]), and the upper critical fields (Hₘ) is estimated of 0.89 T by using the Ginzburg-Landau function. On the other hand, at high temperature range, EuSn₂As₂ exhibits a metallic behavior, the resistivity-pressure curve (at 150 K) shows two discontinuous change points near 5 and 12.6 GPa, respectively, correspond to the two-stage structural conversion process. These discoveries spread respectively between the buckled SnAs bilayers. Meanwhile, electrical transport measurements revealed an insulator-metal-superconductor transition at low temperature around 5 and 15 GPa, respectively, correspond to the two-stage structural conversion process. These discoveries spread over the research fields of superconductivity, topological insulators, and quantum magnetism, and thus will provide a new venue for studying various topics of current condensed matter physics.

As shown in Fig. 4(a) and 4(b), with increasing pressure, Tₐ monotonously increases from 25.4 K at 0.77 GPa to 86 K at 14 GPa. Similar increasing behavior of Tₐ under pressure has been also observed in recently reported magnetic topological insulator EuIn₂As₂ [55], but no structural phase transitions and superconductivity are observed up to 17 GPa in the crystalline EuIn₂As₂.

In summary, we have identified a new monoclinic EuSn₂As₂ structure in C2/m symmetry above ~14 GPa by ab initio calculations and in situ XRD measurements. This distinct monoclinic phase has a three-dimensional network structure comprising honeycomblike Sn sheets and zigzag As chains, transformed from the layered rhombohedral structure via a two-stage reconstruction mechanism with the connecting of Sn-Sn and As-As atoms successively between the buckled SnAs bilayers. Meanwhile, electrical transport measurements revealed an insulator-metal-superconductor transition at low temperature around 5 and 15 GPa, respectively, correspond to the two-stage structural conversion process. This work was supported by the National Key R&D Program of China (Grants No. 2016YFA0401503, No. 2016YFA0300604, No. 2018YFA0305700, No. 2018YFA0305900, and No. 2020YFA0711502), the National Natural Science Foundation of China (Grants No. 11974387, No. 12004416, No. 11674328, No. U2032204, No. 11774126, No. 12004014, No. U1832123, and No. U1930401), the Strategic Priority Research Program and Key Research Program of Frontier Sciences of the Chinese Academy of Sciences (Grants No. XDB33000000, No. XDB25000000, and No. QYZDBSSW-SLH013), the K.C. Wong Education Foundation (No. GJTD-2018-01), and the Youth Innovation Promotion Association of Chinese Academy
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[44] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.126.155701 for the detailed computational and experimental methods; the single crystal and powdered XRD pattern of EuSn$_2$As$_2$ at ambient pressure (Fig. S1); the simulated XRD pattern for $\alpha$- and $\beta$-EuSn$_2$As$_2$ at various pressure (Fig. S2); the refined lattice parameters and atomic coordinates for EuSn$_2$As$_2$ at various pressure (Table S1); the temperature-dependent resistance at various magnetic filed (Fig. S3); and the temperature-pressure phase diagram of EuSn$_2$As$_2$ (Fig. S4). The Supplemental Material includes Refs. [14,37–43,45–52].